

# Phase evolution criteria for AlCoCrCuFeMnSix ( $x = 0, 0.3, 0.6$ and $0.9$ ) high entropy alloys based on experiment and thermodynamic calculation

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**Abstract.** Present study investigates the phase evolution behaviour of AlCoCrCuFeMnSix ( $x = 0, 0.3, 0.6$  and  $0.9$ ) high entropy alloys, synthesized by mechanical alloying and arc melting. The phase evolution, microstructure, and mechanical properties were analysed to understand the effect of Si addition in AlCoCrCuFeMn high entropy alloy. The X-ray diffraction, after 15h mechanical alloying, reveals the mixture of body-centered and face-centered cubic structure. The addition of Si favours body-centered cubic structure formation during mechanical alloying. The phase evolution observed after XRD are in accord with the thermodynamically predicted phases.

## 1. Introduction

High Entropy Alloys or HEAs for short, are alloying frameworks made out of no less than 5 components. The idea of HEAs was presented by Achard in the late of eighteen century, further, in the mid of 1900s, Yeh and his partners investigated the universe of multi-component alloy [1]. The extraordinary capacity of HEAs to form often single solid solution with their incredible properties, for example, wear resistance, high hardness, softening resistance at higher temperature, corrosion and oxidation resistance have made tremendous enthusiasm among scientists.

Previous literatures suggests that researchers mainly focused on the improvement of mechanical properties of HEAs by varying the content of any one transition element of the composition. Though, limited studies have been reported the effect of non-metallic element such as Si addition and their influence on the phase evolution and mechanical properties. As Si is always favourable for structural and mechanical properties in conventional materials like steel. Liu et al., [2] observed that increasing the Si content on Al<sub>0.5</sub>CoCrCuFeNiSi<sub>x</sub> ( $x = 0, 0.4, 0.8$ ) endorses the BCC phase evolution compared to FCC phase. A substantial improvement in wear resistance was reported with increase in Si contents because of high negative enthalpy of mixing between Si and other elements of composition. Kumar et al., [3] also observed that, with increase in amount of Si from 0 to 0.9, facilitates the BCC phase formation over FCC phase. Therefore, in the present study, the effect of Si on the phase evolution characteristic of AlCoCrCuFeMnSix ( $x = 0, 0.3, 0.6, 0.9$ ) HEAs, synthesized by mechanical alloying and arc melting were investigated.

Since the principal reports of high entropy alloys (HEAs), various endeavours have been made to foresee phase evolution in these alloys, specifically to predict compositions, which would support



evolution of solid solution phases. Despite the fact that advancement of alloys based on the multiple elements with equiatomic or near to equiatomic ratio without a doubt broadened the perspective of materials researchers on the plan of new materials, the role of entropy for the formation of solid solution not be over-underlined. Initially, it is suggested that the higher entropy of mixing results into the formation of solid solution phase [4] as expressed in equation (1).

$$(\Delta S_{mix}) = -R \sum_{i=1}^n C_i \ln C_i \quad (1)$$

Where R is the gas constant (8.314 J/ mol. K),  $C_i$  is the atomic fraction of element i and n is the number of components. From the above equation, the high  $\Delta S_{mix}$  can significantly lower the free energy, in this way bringing down the affinity to order and segregate, which accordingly makes solid solution more effectively form and more stable than intermetallic. However, disregarding having high  $\Delta S_{mix}$  values, many HEAs are multi-phase and can likewise contain IM phases [5].

A few extra-empirical criteria for anticipating solid solution phase formation in HEAs were presented as of late [6]. Like Hume-Rothery rules for substitutional solid solutions, these criteria concentrate on the atomic size difference ( $\delta$ ), mixing enthalpy ( $\Delta H_{mix}$ ), electronegativity ( $\Delta \chi$ ), valence electron concentration (VEC) and a parameter  $\Omega$  were also used to develop criteria for the stability of SS, IM and/or amorphous phases in as-cast HEAs. Equations reported by Dong et al., [7] and Zhang et al., [8] has been used to calculate the design parameters.

Another important parameter formulated by Mansoori et al., [9] based on the mismatch entropy for bulk metallic glasses was also used in the present study for phase formation prediction and is given as (equation (2)).

$$\frac{\Delta S_{\sigma}}{k} = \left[ \frac{3}{2}(\zeta - 1)y_1 + \frac{3}{2}(\zeta - 1)^2 y_2 - \left\{ \frac{1}{2}(\zeta - 1)(\zeta - 3) + \ln \zeta \right\} (1 - y_3) \right] \quad (2)$$

To verify all these design parameters for phase prediction criterion, a series of AlCoCuCrFeMnSix (x = 0, 0.3, 0.6 and 0.9) HEAs were prepared through MA. The calculated values of these design parameters are listed in table 2. The aim of the present study is to analyze the effect of Si on AlCoCrCuFeMn HEAs and to confirm the phase evolution based on the previously developed thermodynamic calculation for the HEA.

## 2. Materials and methods

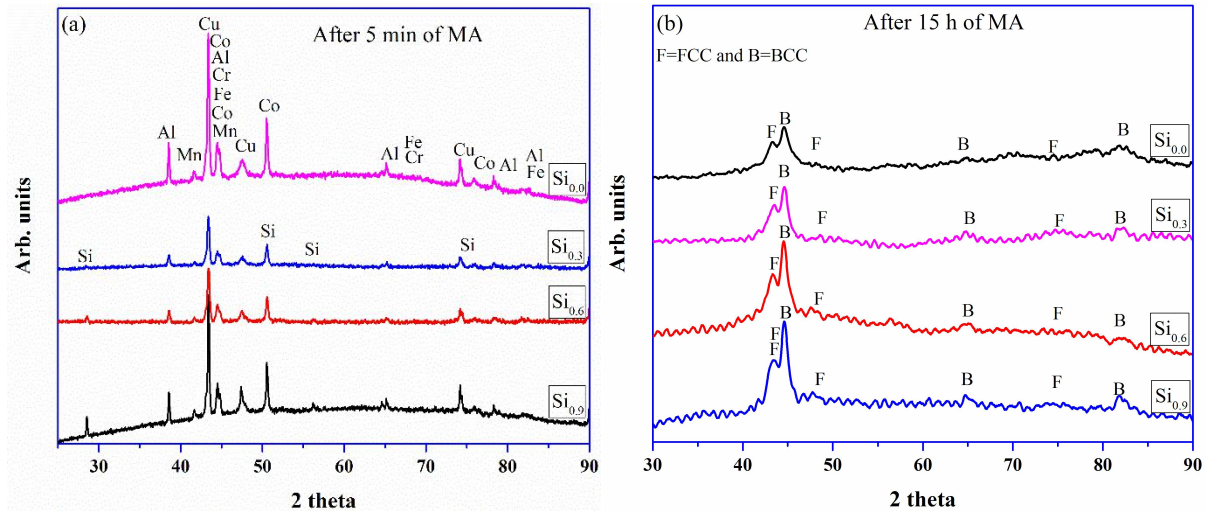
The elemental powders of Al, Co, Cu, Cr, Fe, Ni, and Si were mechanically alloyed for 15 h to prepare HEAs. High energy ball mill (HEMB) (Retsch: PM-400) was used for milling the powder. The ball to powder ratio was 10:1 with 250 ml capacity tungsten carbide vials and 10 mm diameter balls. The rotation speed of 300rpm was set throughout the milling process. Phase evolution are characterized through X-ray diffractometer (XRD, PANALYTICAL, X' pert powder) with Cu K $\alpha$  radiation. Finally, the experimental results were compared with the thermodynamic parameters.

Pseudo-Voigt function was used for fitting XRD peak profile. The crystallite sizes and lattice strain of the milled powders were calculated based on Scherrer's formula [10] from XRD peaks and Si was used as the standard sample to subtract the instrumental broadening.

## 3. Results and discussions

Figure 1 shows the XRD peaks obtained during mechanical alloying of AlCoCuCrFeMnSix powders, as a function of milling time. For as milled samples, the crystalline peaks for principal elements are observed before 5 h. As the milling time increases, the intensities of XRD peaks of pure constitutional elements decreases, which indicates dissolution of pure elements. In addition, further milling of the powder leads to overlapping of peaks to each other compared with the beginning of the milling. From the diffraction pattern it is evident that, after 15 h of milling, mixture of FCC and BCC phase were obtained.

The decrease in intensities and disappearance of most of the XRD peaks by increasing the milling time might be due to the crystal size refinement, higher lattice strain and the formation of solid solution[11].



**Figure 1.** XRD patterns of (a) AlCoCrCuFeMn and (b) AlCoCrCuFeMnSi<sub>0.3</sub> (c) AlCoCrCuFeMnSi<sub>0.6</sub> (d) AlCoCrCuFeMnSi<sub>0.9</sub> mechanical alloyed powders at different time intervals.

The crystallite size and lattice strain are illustrated in Table 1. The increase in milling time during mechanical alloying, contributed to decrease in crystallite size of BCC phase, reaching 24, 21, 20 and 16 nm for the value of  $x = 0, 0.3, 0.6$  and  $0.9$  respectively. No significant change observed in the crystalline size with increase in milling time from 10 h to 15 h. The regular increase in the lattice strain observed with increase in the milling time, which have constructive impact on the solid solution strengthening. The increase in lattice strain is attributed to (1) mismatch effect of size between constituent elements, as Si has small atomic radius compared to other elements in the compositions, (2) increase in grain boundary fraction and (3) mechanical deformation [12,13]. Growth in dislocation density due to severe plastic deformation also contributes to higher lattice strain [14].

**Table 1.** Crystallite size (CS) and lattice strain (LS) of BCC phase in AlCoCrFeNiSix ( $x = 0, 0.3, 0.6, 0.9$ ) high entropy powder with milling time.

Milling time (h)	AlCoCrCuFeMn		AlCoCrCuFeMnSi <sub>0.3</sub>		AlCoCrCuFeMnSi <sub>0.6</sub>		AlCoCrCuFeMnSi <sub>0.9</sub>	
	CS (nm)	LS (%)	CS (nm)	LS (%)	CS (nm)	LS (%)	CS (nm)	LS (%)
5	82	0.89	79	1.12	77	1.18	72	1.51
10	24	2.70	21	2.84	20	2.91	16	2.97
15	25	2.81	21	2.90	21	2.94	16	2.99

To verify the phase evolution during mechanical alloying, mixing entropy ( $\Delta S_{\text{Mix}}$ ), mixing enthalpy ( $\Delta H_{\text{Mix}}$ ), valence electron concentration (VEC), atomic size mismatch ( $\delta$ ), electronegative difference ( $\Delta\chi$ ),  $\Omega$  and mismatch entropy  $\Delta S_o/k$  in HEA according to Hume- Ruthery rule have been calculated and shown in Table 2.

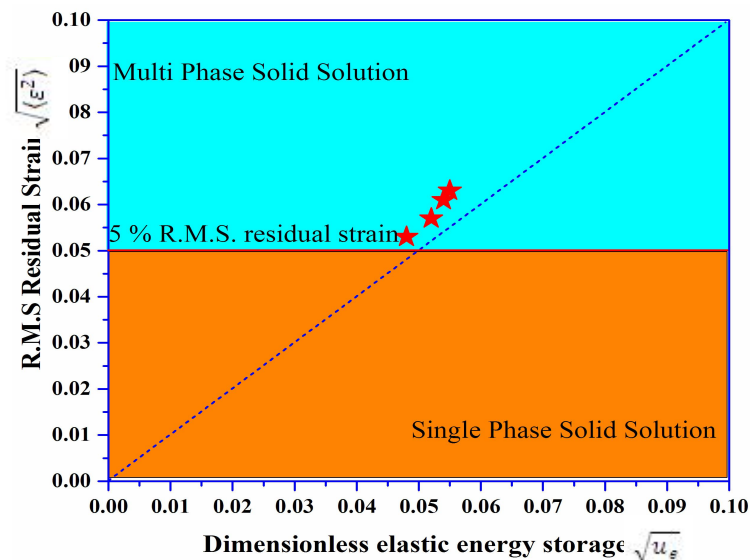
Guo et al. investigated the effect of valence electron concentration (VEC) for the solid solution formation on HEA. They observed that BCC phase will be stable at  $\text{VEC} \leq 6.8$  whereas, for  $6.8 \leq \text{VEC} \leq 8$  mixed phases of BCC and FCC occurs [15]. The above-discussed phase prediction criteria based on the VEC is in accord with the alloys studied in this work. The criteria given by Yang et al. based on the atomic size mismatch ( $\delta$ ) for the prediction of stabilized solid solution ( $\delta \leq 6.6\%$ ) also satisfied in the present studied alloys. Furthermore, the range of  $\Delta\chi$  values for the prediction of solid solution phase formation calculated by Guo and Liu also satisfied by alloys prepared in this study [16].

Liu and Yang et al defined a new parameter  $\Omega$  to classify solid solution phases and intermetallic, they observed that, if  $\Omega > 1$ , the solid solution formation will be more and if  $\Omega \leq 1$  intermetallic compound formation occurs. This criteria is also satisfied in the present alloys.

Raghvan et al.[17] suggested that the BCC phase is favoured than the FCC phase for the high value of  $\Delta S_\sigma/k$  and correspondingly less value of  $\Delta H_{mix}$ . Intermediate values of  $\Delta S_\sigma/k$  and  $\Delta H_{mix}$  were accepted for mixture of BCC and FCC phases.

**Table 2.** Calculated parameters  $\Delta H_{mix}$ ,  $\Delta S_{mix}$ , VEC,  $\delta$ ,  $\Delta\chi$ ,  $\Omega$ ,  $\Delta S_\sigma/k$ ,  $\sqrt{\langle \epsilon^2 \rangle}$  and  $\sqrt{u_e}$  for prepared HEAs.

Alloys	$\Delta S_{Mix}$	$\Delta H_{Mix}$	VEC	$\delta$ %	$\Delta\chi$	$\Omega$	$\Delta S_\sigma/k$	$\sqrt{\langle \epsilon^2 \rangle}$	$\sqrt{u_e}$
AlCoCrCuFeMn	14.89	-3.77	7.3	5.33	0.1372	6.28	0.047	0.053	0.048
AlCoCrCuFeMnSi <sub>0.3</sub>	15.77	-9.26	7.1	5.77	0.1381	2.72	0.054	0.057	0.052
AlCoCrCuFeMnSi <sub>0.6</sub>	16.07	-13.75	7.0	6.10	0.1386	1.87	0.060	0.061	0.054
AlCoCrCuFeMnSi <sub>0.9</sub>	16.17	-17.44	6.8	6.36	0.1389	1.48	0.070	0.063	0.055



**Figure 2.** The R.M.S. residual strain and dimensionless elastic energy storage.

Additionally, to verify the phase formation in HEAs after mechanical alloying we have also implemented newly proposed geometric model based on the atomic stress theory proposed by Ye et al., [18]. Ye et al. considered the root mean square residual strain ( $\sqrt{\epsilon^2}$ ) and square root of dimensionless elastic energy storage ( $\sqrt{u_e}$ ) to classify single phase, multi-phase for as-cast HEAs and compared results with experimental observations. First time, an effort has been made in the present study to extend the model proposed by Ye et al. on the high entropy alloys prepared by mechanical alloying process (Table 2).

Ye et al. extended the Lindemann benchmarks to single and multi-phase alloys. It is claimed that at 5% residual strain, single phase solid solution converts into multi-phase solid solution. During this conversion, all the strain is not released. The extension of Ye et al. theory, which was proposed for HEA alloys prepared by casting route also holds good for HEAs prepared by mechanical alloying route (Figure 2).

#### 4. Conclusion

The AlCoCrCuFeMnSi<sub>x</sub> HEA alloys with different Si content ( $x = 0, 0.3, 0.6$  and  $0.9$ ) were successfully synthesized via mechanical alloying. During MA, solid solution mixture of BCC and FCC structure formed after 15h of milling. The valence electron concentration, mixing enthalpy, atomic size difference, electronegativity and mismatch entropy play significant role to control FCC and BCC phase formation. It is important to point out that calculation of design parameter for composition under consideration are in good accord with the reported data in literature for solid solution formation. The relationship between experimental data and calculated data is in agreement with model based on the R.M.S. residual strain and dimensionless elastic energy storage. This correlation suggests that conversion from single phase to multi-phase structure occurs at around  $\sim 5\%$  R.M.S. residual strain.

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